

HL - Organic Reactions 20.1-20.3

IB Chemistry
T20D01

Mr. Martin Brakke



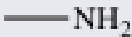
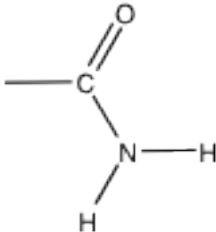
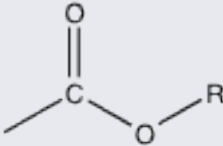

20.1 - Introduction

- 20.1.1 Deduce structural formulas for compounds containing up to six carbon atoms with one of the following functional groups: amine, amide, ester and nitrile. (3)
- 20.1.2 Apply IUPAC rules for naming compounds containing up to six carbon atoms with one of the following functional groups: amine, amide, ester and nitrile. (2)



Further Structural Formulas

20.1.1 Deduce structural formulas for compounds containing up to six carbon atoms with one of the following functional groups: amine, amide, ester and nitrile. (3)

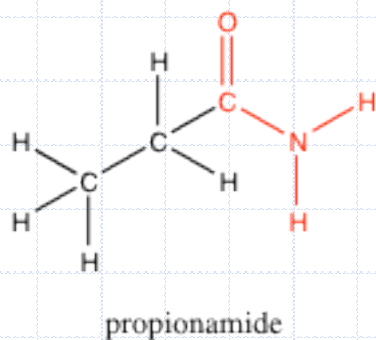
Name	Functional Group	Suffix in IUPAC name	Example of compound
Amine*		-anamine	$\text{C}_3\text{H}_7\text{NH}_2$ propanamine
Amide*		-anamide	$\text{C}_2\text{H}_5\text{CONH}_2$ propanamide
Ester		-anoate	$\text{C}_2\text{H}_5\text{COH}_3$ methyl propanoate
Nitrile (HL)		-anenitrile	$\text{C}_2\text{H}_5\text{CN}$ propanenitrile

IUPAC of Further Formulas

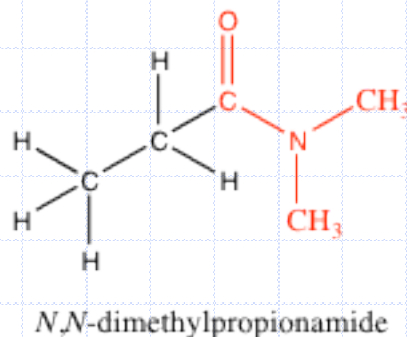
20.1.2 Apply IUPAC rules for naming compounds containing up to six carbon atoms with one of the following functional groups: amine, amide, ester and nitrile. (2)

- **Amides:** Amides are **acid derivatives** where the -OH of the acid has been replaced by -NX_2 . Primary amides have an -NH_2 group; secondary and tertiary amides are substituted with respectively one and two alkyl groups bonded to the nitrogen. In these cases the substituent groups are named using N- and N,N- before the substituent.

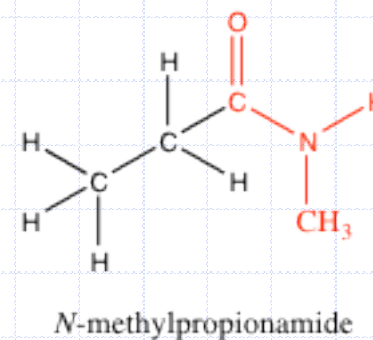
Primary amide..



Tertiary amide..



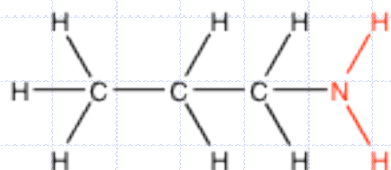
Secondary amide..



Amine Functional Group

- Primary amines have an -NH_2 group which can undergo substitution by alkyl groups, giving rise to secondary and tertiary amines. These are named in a similar way to the amides, using N- to show the position of the substituents

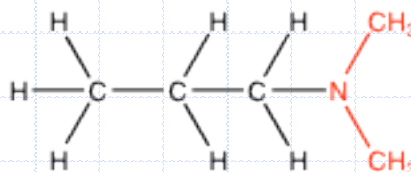
Primary amine..



propan-1-amine

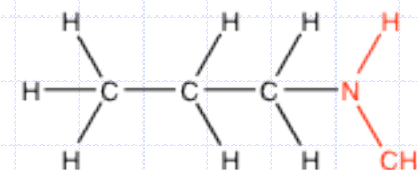


Tertiary amine..



N,N-dimethylpropan-1-amine

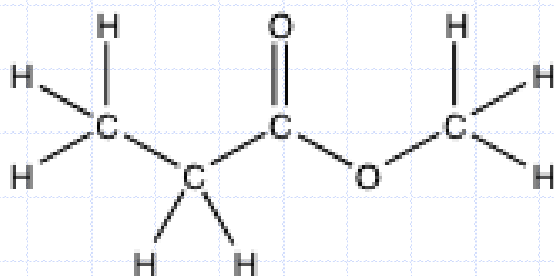
Secondary amine..



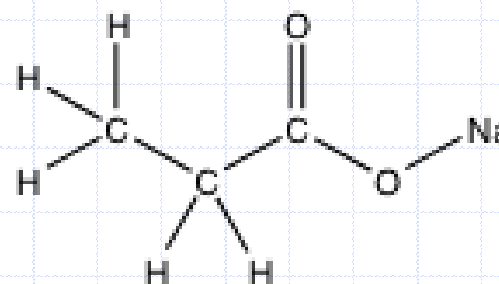
N-methylpropan-1-amine

Ester Functional Group

- Esters are organic salts where the alkyl group of the alcohol has replaced the hydrogen of the carboxylic acid. Their name puts the alkyl group first followed by the name of the acid anion, for example:



methyl propionate

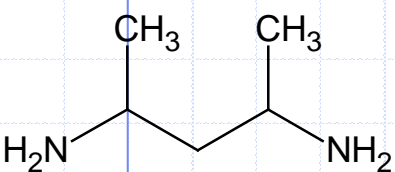


sodium propionate

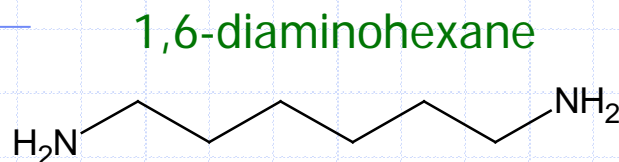


IUPAC for

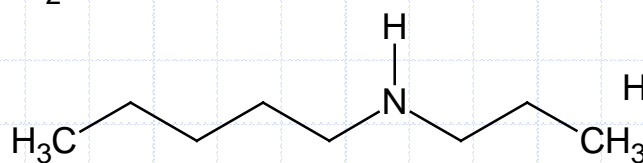
Amines



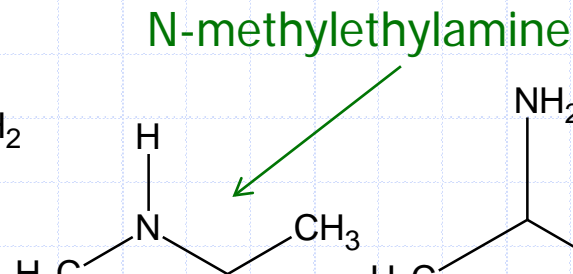
2,4-diaminopentane



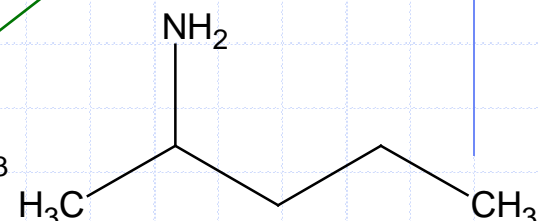
1,6-diaminohexane



N-propylpentylamine

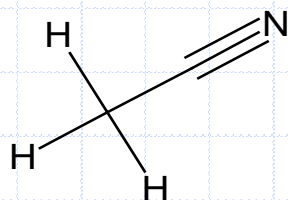


N-methylethylamine

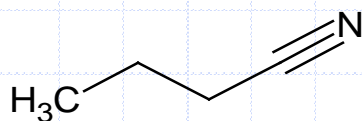


2-aminopentane

Nitriles

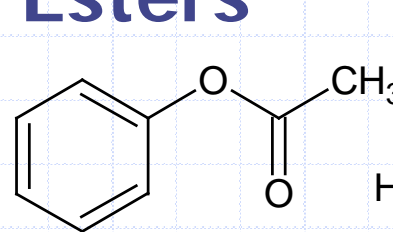


ethanenitrile

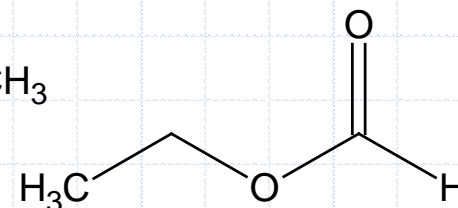


butanenitrile

Esters

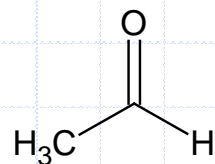


Phenyl ethanoate

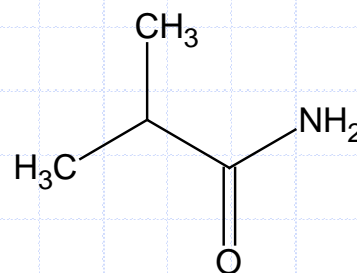


Ethyl methanoate

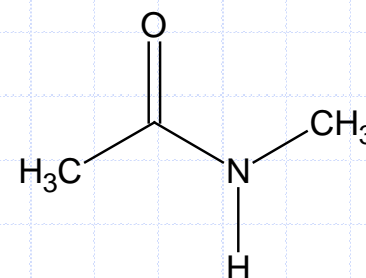
Amides



ethanamide



2-methylpropanamide



N-methylethanamide



20.2 – Nucleophilic Substitution Reactions

- 20.2.1 Explain why the hydroxide ion is a better nucleophile than water. (3)
- 20.2.2 Describe and explain how the rate of nucleophilic substitution in halogenoalkanes by the hydroxide ion depends on the identity of the halogen. (3)
- 20.2.3 Describe and explain how the rate of nucleophilic substitution in halogenoalkanes by the hydroxide ion depends on whether the halogenoalkane is primary, secondary or tertiary. (3)
- 20.2.4 Describe, using equations, the substitution reactions of halogenoalkanes with ammonia and potassium cyanide. (2)
- 20.2.5 Explain the reactions of primary halogenoalkanes with ammonia and potassium cyanide in terms of the S_N2 mechanism. (3)
- 20.2.6 Describe, using equations, the reduction of nitriles using hydrogen and a nickel catalyst. (2)



Nucleophiles: OH^- vs H_2O

20.2.1 Explain why the hydroxide ion is a better nucleophile than water. (3)

- The nucleophile is the species attracted to the partially positive carbon atom (δ^+) that is bound to the electronegative halogen atom
- Effective Nucleophiles
 - Neutral or negatively charged containing lone pair of e^-
 - The more dense the charge is, the better
 - Less electronegative nucleophiles are better, thus NH_3 is better than H_2O
 - OH^- has 3 lone pairs, compared to 2 from H_2O
 - ◆ The less electronegative can more easily donate its pair of electrons



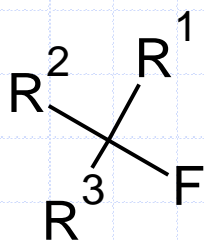
decreasing nucleophilic strength

Rate of S_N Reactions

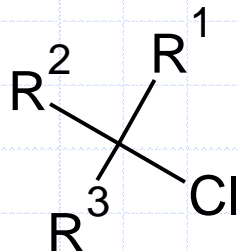
20.2.2 Describe and explain how the rate of nucleophilic substitution in halogenoalkanes by the hydroxide ion depends on the identity of the halogen.

- In order for the S_N reactions to occur, carbon-halogen bond must be weak enough (relative strength is key)

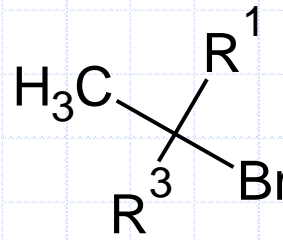
Worst Leaving group



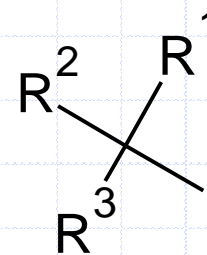
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Best Leaving group

Bond Enthalpy
kJ mol⁻¹

484

338

276

238

- This may be confusing as F is most electronegative, therefore it has the most ionic character, making the (δ^+) nucleophile more electron deficient and polar. You might predict that F would be most reactive



But, experimental evidence show that the polarity of the C-halogen bond is not nearly as important as the strength of the C-halogen bond

Rate of S_N based on 1° , 2° , or 3°

20.2.3 Describe and explain how the rate of nucleophilic substitution in halogenoalkanes by the hydroxide ion depends on whether the halogenoalkane is primary, secondary or tertiary. (3)

- Primary halogenoalkanes: S_N2
 - Single step with a transition state
- Secondary halogenoalkanes: S_N1 / S_N2
- Tertiary halogenoalkanes: S_N1
 - 2-step with a stable intermediate carbocation
- Rate of Reactions
 - S_N1 reactions > S_N2 reactions
 - For S_N1 ; tertiary > secondary > primary due to stability

Primary

Secondary

Tertiary

carbocations increase in stability



S_N Reactions with NH_3 and CN^-

20.2.4 Describe, using equations, the substitution reactions of halogenoalkanes with ammonia and potassium cyanide. (2)

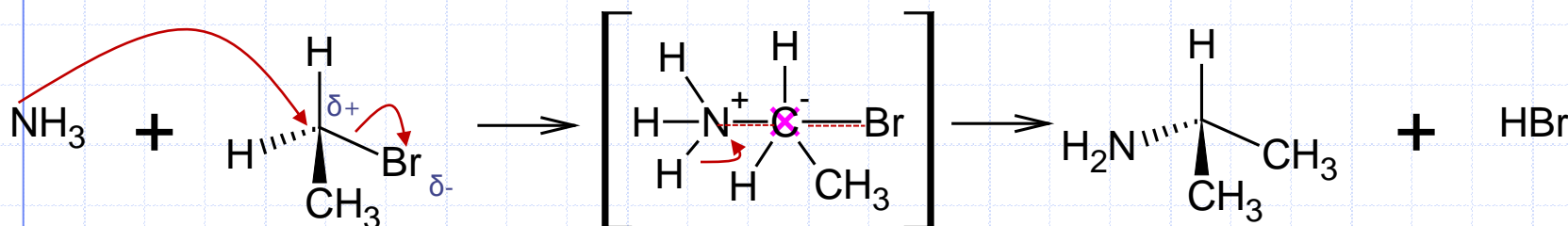
- Ammonia can act as a nucleophile just as OH^- and H_2O
 - The lone pair on N allows the compound to attack the electrophile (electron deficient carbon)
 - $CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_2 + HBr$
 - ◆ This product still contains lone pairs on the N, so yes, it can continue to act as a nucleophile
- Cyanide can act as a nucleophile as well
 - Once again, the lone pair on N allows the compound to attack the electrophile (electron deficient carbon)
 - $CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$



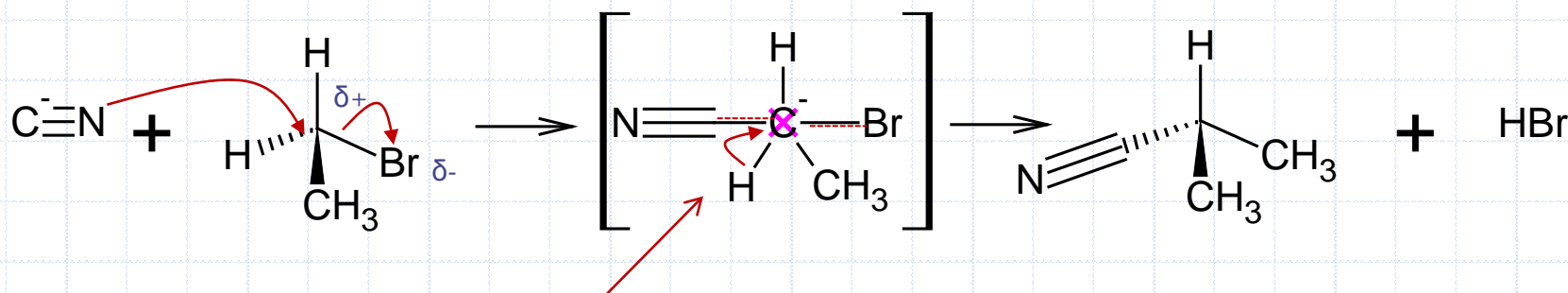
Mechanism of S_N2 with KCN and NH_3

20.2.5 Explain the reactions of primary halogenoalkanes with ammonia and potassium cyanide in terms of the S_N2 mechanism. (3)

Mechanism of S_N2 with NH_3



Mechanism of S_N2 with KCN



The Carbon should not be crossed out, the program used does not allow for a proper intermediate to be drawn. The bonds should be dashed as the halogen leaves and the nucleophile attacks.



20.2.6 Describe, using equations, the reduction of nitriles using hydrogen and a nickel catalyst. (2)

- Nitriles are common in organic synthesis bc:
 - Can be synthesized from a halogenalkane
 - Can be reduced using hydrogen gas (Ni cat) to form amines
 - $\text{CH}_3\text{CH}_2\text{CN} + 2\text{H}_2 \text{ (Ni cat)} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$
- They can also be hydrolyzed in acidic solutions to form carboxylic acids
 - $\text{CH}_3\text{CH}_2\text{CN} + \text{H}_2\text{O} \text{ (H}_2\text{SO}_4 \text{ cat)} \rightarrow \text{CH}_3\text{CH}_2\text{COOH} + \text{NH}_4^+$



20.3 – Elimination Reactions

- 20.3.1 Describe, using equations, the elimination of HBr from bromoalkanes. (2)
- 20.3.2 Describe and explain the mechanism for the elimination of HBr from bromoalkanes. (3)



Elimination Reactions

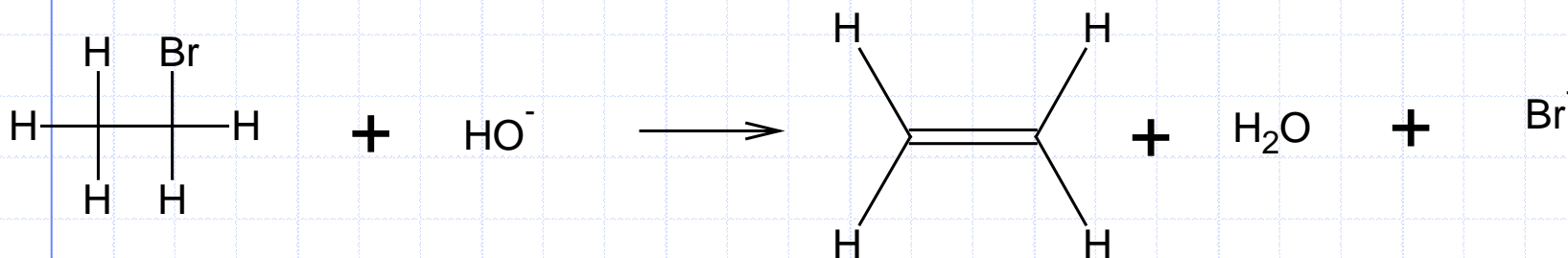
- As described in the 10.3 introduction to various organic reactions, an elimination reaction is described as:
 - Occurs when a small molecule is lost from a larger compound
 - Usually results in the formation of a double or triple bond
 - When the molecule eliminated is H_2O , the reaction is **dehydration**
 - For example: $\text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O}$



Elimination of HBr from Br-alkanes

20.3.1 Describe, using equations, the elimination of HBr from bromoalkanes. (2)

- To generalize the elimination of HBr:



- Favored Conditions:
 - NaOH or KOH dissolved in hot ethanol (less polar than H₂O)
 - Elimination favored by tertiary halogenalkanes
 - Heated under reflux



Equations for Br Elimination

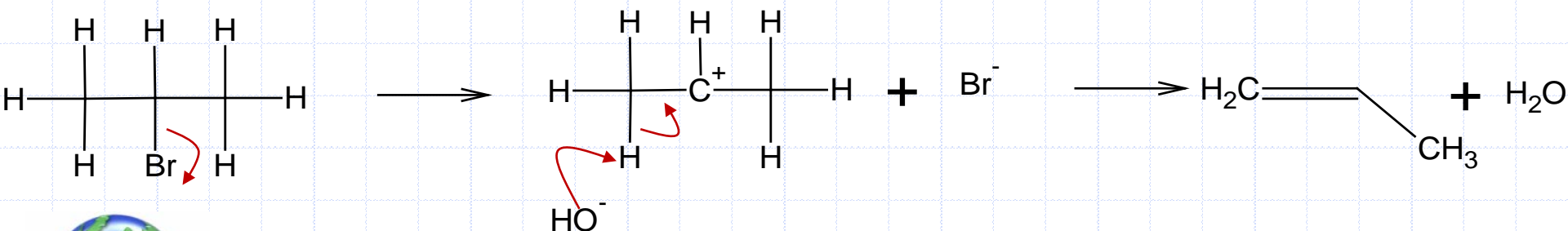
- Equations for elimination of Br from short chains:
 - $\text{CH}_3\text{CH}_2\text{Br} + \text{KOH} \rightarrow \text{CH}_2=\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} + \text{KOH} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$
 - $\text{CH}_3\text{CHBrCH}_3 + \text{KOH} \rightarrow \text{CH}_3\text{CH}=\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$
- As chains **get longer**, multiple variations of products are possible
 - $\text{CH}_3\text{CH}_2\text{CHBrCH}_3 + \text{KOH} \rightarrow$
 $\text{CH}_3\text{CH}=\text{CHCH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{KBr} + \text{H}_2\text{O}$



Mechanism of HBr Elimination

20.3.2 Describe and explain the mechanism for the elimination of HBr from bromoalkanes. (3)

- The mechanism for the elimination of HBr can be E1 or E2 (similar to S_N1 and S_N2)
 - E1 = 1st order reaction
 - E2 = 2nd order reaction
- E1 mechanism proceeds through a carbocation intermediate (like S_N1) and involves the heterolytic fission of the C-Br bond



♦ Secondary and Tertiary bromoalkanes favor this reaction, just as in S_N1

E2 Mechanism for Elimination of HBr

- The E2 Mechanism involves the OH^- nucleophile attacking along with other mechanisms in one single step:
 - OH^- removes H^+ ion
 - Lone pair of e^- left on carbon shifts to form a double bond
 - The Br atom leaves as a Br^- ion

